

Magnetic Field versus Temperature Phase Diagram of the Spin-1/2 Alternating Chain Compound F₅PNN

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We have measured the specific heat of the $S = 1/2$ alternating Heisenberg antiferromagnetic chain compound pentafluorophenyl nitronyl nitroxide in magnetic fields using a single crystal and powder. A sharp peak due to field-induced magnetic ordering (FIMO) is observed in both samples. The H - T phase boundary of the FIMO of the single crystal is symmetric with respect to the central field of the gapless field region $H_{C1} \leq H \leq H_{C2}$, whereas it is distorted for the powder whose ordering temperatures are lower. An analysis employing calculations based on the finite temperature density matrix renormalization group indicates the possibility of novel incommensurate ordering due to frustration in the powder around the central field.

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I. INTRODUCTION

Field-induced magnetic ordering (FIMO) in spin-gapped systems, in which an energy gap exists for low-lying excited states, has been investigated in a vast number of compounds, particularly in the context of the Bose-Einstein condensation (BEC) of triplet magnons¹. The BEC picture is useful for understanding the nature of the FIMO with the commensurate (C) antiferromagnetic order perpendicular to the field direction. Recently, Suzuki *et al.* and Maeshima *et al.* have added a new aspect to the FIMO on the basis of numerical analyses combined with field theories^{2,3}. These authors have predicted that a magnetic field induces a novel incommensurate (IC) order parallel to the field direction in $S = 1/2$ alternating chains with a frustrated next-nearest-neighbor (NNN) interaction. Around the central field of the field-induced Tomonaga-Luttinger liquid (TLL) phase of this system between the lower and upper critical field, H_{C1} and H_{C2} , frustration changes the dominant spin correlation from C to IC. If small inter-chain interactions exist, the dominant IC correlation leads to long-range IC ordering in the field direction. In the case frustration is not strong enough to stabilize the IC order at high temperatures, a first order phase transition will happen from the BEC to the IC order at very low temperatures^{3,4}.

The theoretical studies mentioned above^{2,3} have been stimulated by experimental works on the organic radical compound pentafluorophenyl nitroxide (F₅PNN)^{5,6,8,9}. The magnetism of F₅PNN arises from unpaired electrons delocalized around the NO moieties. Although this compound has a uniform chain structure at room temperature, the magnetic susceptibility and the magnetization

curve at low temperatures are well reproduced by calculations for an $S = 1/2$ alternating chain model which is described by the spin Hamiltonian⁵;

$$H = -2J \sum_i^{N/2} (S_{2i-1} \cdot S_{2i} + \alpha S_{2i} \cdot S_{2i+1}). \quad (1)$$

Here, S denotes the $S = 1/2$ Heisenberg-type spin operator, N is the total number of spins, and α is the alternation ratio between competing two nearest-neighbor interactions in a one-dimensional chain. When $\alpha=1$, the system becomes a uniform chain, whereas when $\alpha=0$ the system breaks up into the assembly of isolated dimers. In Ref. 5, the alternation ratio $\alpha = 0.4$ and exchange interaction $2J/k_B = -5.6$ K were obtained for F₅PNN.

The lower and upper critical fields of F₅PNN are determined to be about $H_{C1} = 3.0$ T and $H_{C2} = 6.5$ T from the magnetization curve. NMR shows a TLL behavior in spin-lattice relaxation and provides evidence for a NNN interaction^{6,7,8}. In previous works, we observed FIMO by measuring the specific heat of a polycrystalline sample in magnetic fields up to 8.0 T ($> H_{C2}$)¹⁰. Above the critical temperature of the FIMO, the temperature dependence of the specific heat $C(T)$ in magnetic fields was in good qualitative agreement with a numerical calculation which assumes the TLL^{10,11}.

In this paper, we present the H - T phase diagrams of a single crystal and powder of F₅PNN obtained from detailed specific heat measurements in magnetic fields. Reentrant H - T phase diagrams for the FIMO phase are obtained for both samples. However, the shape of the phase boundary depends on the form of the sample. That of the single crystal is symmetric with respect to a cen-

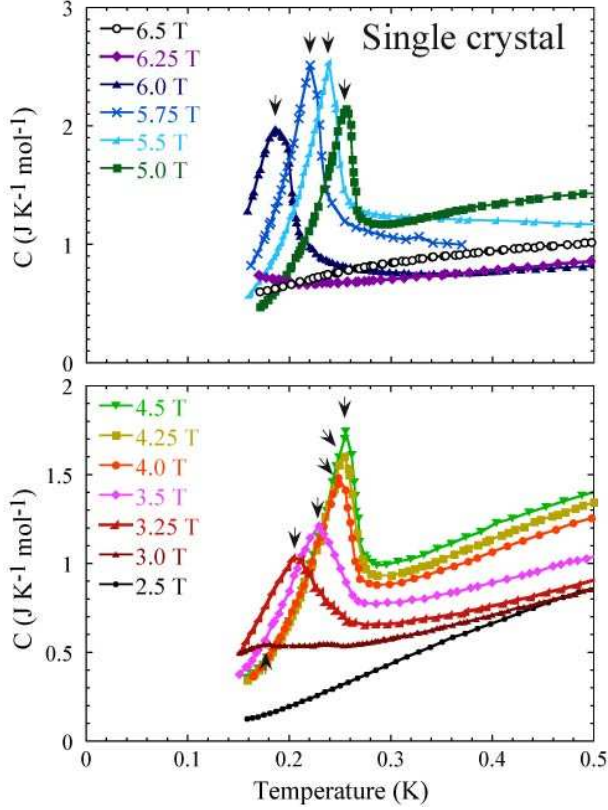


FIG. 1: (color online) Specific heat of the single crystal in magnetic fields. Arrows indicate peak temperatures of the FIMO. Upper panel: $5.0 \text{ T} \leq H \leq 6.5 \text{ T}$. Lower panel: $2.5 \text{ T} \leq H \leq 4.5 \text{ T}$.

tral field of the gapless field region between H_{C1} and H_{C2} , whereas the powder has a phase boundary which is distorted and pushed to lower temperatures than that of the single crystal.

II. EXPERIMENTAL PROCEDURES

F₅PNN was prepared using the method described in Ref. 12. Specific heat measurements were performed by the adiabatic heat-pulse method using a ³He-⁴He dilution refrigerator. The powder sample was mixed with Apiezon N grease to ensure good thermal contact, and was mounted on the sample cell in the refrigerator. The single crystal sample was attached to the cell with the same grease. The nuclear contributions of hydrogen and fluorine to the specific heat were subtracted.

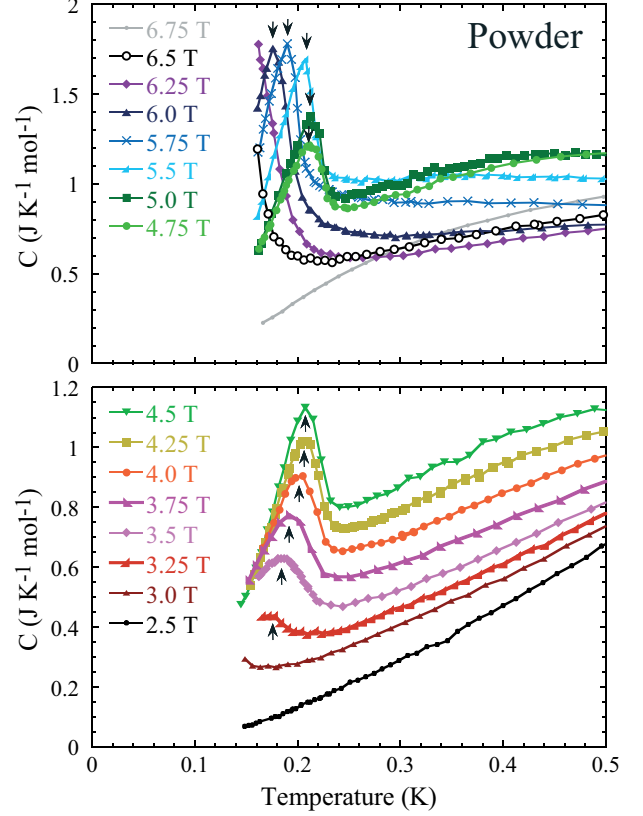


FIG. 2: (color online) Specific heat of the powder in magnetic fields. Arrows indicate peak temperatures of the FIMO. Upper panel: $4.75 \text{ T} \leq H \leq 6.75 \text{ T}$. Lower panel: $2.5 \text{ T} \leq H \leq 4.5 \text{ T}$.

III. RESULTS

Figure 1 shows $C(T)$ of the single crystal in magnetic fields. A sharp peak due to the FIMO is clearly seen in fields between 3.25 T and 6.0 T. A small peak is observed at 3.0 T, and an upturn indicating a peak at a lower temperature at 6.25 T. Also, exponential temperature dependences are observed at 2.5 T and 6.5 T, indicative of energy gaps for low-lying excitations. We conclude from these observations that the critical fields of the single crystal are $H_{C1} \simeq 3.0 \text{ T}$ and $H_{C2} \simeq 6.25 \text{ T}$.

A sharp peak in $C(T)$ is clearly observed also in the powder in fields $3.25 \text{ T} \leq H \leq 6.0 \text{ T}$ as shown in Fig. 2, and the peak temperatures are in accordance with those of our previous results^{9,10}. However, the field and temperature dependences of the peak are quite different from those in the single crystal. As the field increases from 3.5 T, the peak becomes much sharper. The field dependence of the peak temperature is weaker than for the single crystal. At 3.0 T, 6.25 T, and 6.5 T, a sharp upturn is observed indicating a peak at lower temperatures, and exponential behaviors are observed at 2.5 T and 6.75

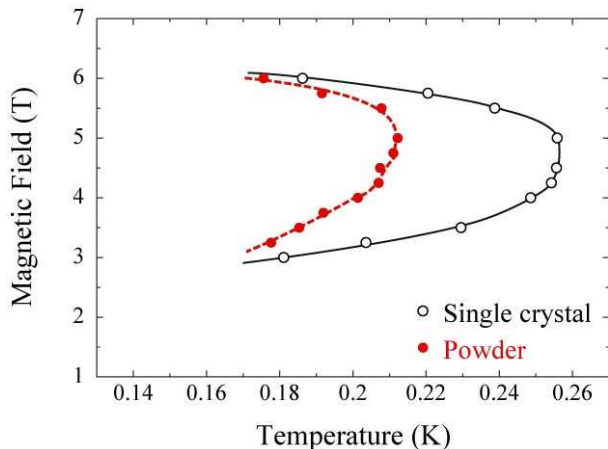


FIG. 3: (color online) Magnetic field versus temperature phase diagram of the single crystal and powder of F_5PNN obtained from the specific heat measurements. Open and filled circles are peak positions of the specific heats of the single crystal and powder, respectively. Solid and broken lines are guides for the eye.

T. Based on these features, the gapless field region of the powder is most likely $3.0 \text{ T} \leq H \leq 6.5 \text{ T}$. This field region is wider than that of the single crystal.

Figure 3 is the H - T phase diagram of the single crystal and powder obtained from the peaks in the specific heat. We note two differences between the H - T phase boundaries for the two sample forms. One is that the peak temperatures are lower for the powder than for the single crystal. The other is a difference in the shape of the phase boundary between the FIMO and paramagnetic phase. The phase boundary of the single crystal is symmetric with respect to the central field of the gapless field region as observed or expected in isotropic spin-gapped compounds investigated so far¹³. In contrast, that of the powder is distorted. Since the peak in $C(T)$ of the powder is sharp even at 6.0 T in Fig. 1(a), it is unlikely that the distinct phase boundary of the powder originates from anisotropy effects. In addition, it is revealed by high-field ESR measurements on the powder sample of this compound that the g -value is almost 2.0 ¹⁴.

IV. DISCUSSION

The observed distorted phase boundary of the FIMO is similar to that of $S = 1/2$ strongly frustrated alternating chain models³. The models exhibit a first-order phase transition at very low temperatures from a conventional field-induced antiferromagnetic order of the spin components perpendicular to the external field direction, which is interpreted as the BEC of triplet magnons, to an IC order along the field direction around the middle of the gapless field region where the IC correlation is dominant. Because frustration suppresses transverse fluctuations, and then decreases the antiferromagnetic ordering

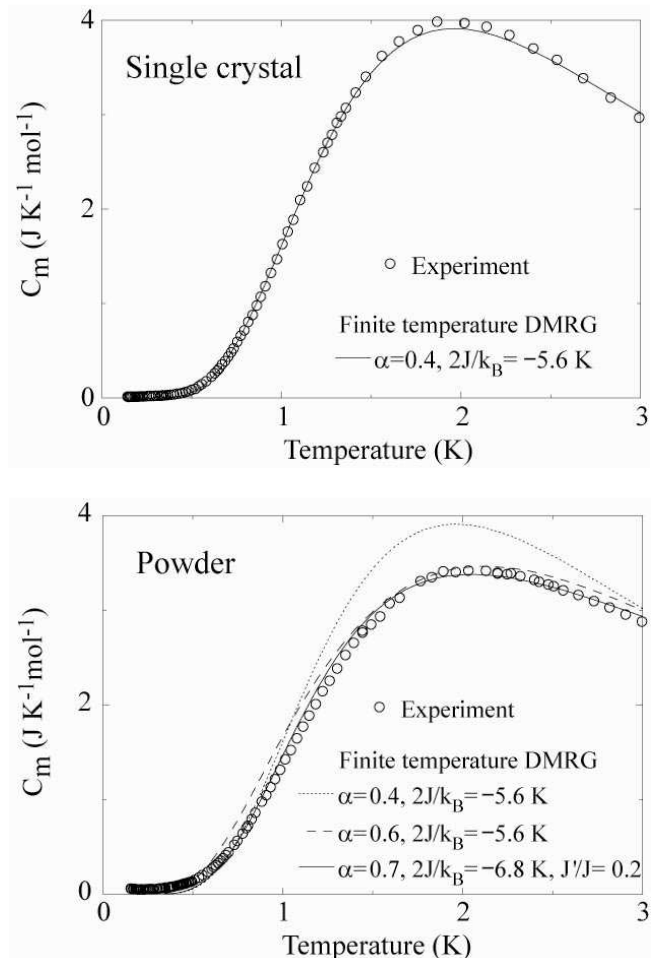


FIG. 4: Temperature dependence of the magnetic specific heats $C_m(T)$ of F_5PNN single crystal and powder at zero field, together with calculated specific heats with three sets of values for the exchange interaction J/k_B and alternation ratio α based on the finite temperature DMRG. Upper panel: the $C_m(T)$ of the single crystal and calculation with $2J/k_B = -5.6 \text{ K}$ and $\alpha = 0.4$. Lower panel: the $C_m(T)$ of the powder and calculations with $2J/k_B = -5.6 \text{ K}$ and $\alpha = 0.4$, $2J/k_B = -5.6 \text{ K}$ and $\alpha = 0.6$, and $2J/k_B = -6.8 \text{ K}$, $J'/J = 0.2$ and $\alpha = 0.7$.

temperature in this field region, the phase boundary for the FIMO is distorted. To argue the possibility that an IC order is realized in the powder, we must first examine if frustration is necessary to explain the powder result.

To determine the exchange interactions J and alternation ratios α of the single crystal and powder, we examine the magnetic specific heat at zero field for both samples. The lattice contribution to the total specific heat is estimated from the data at zero field so that the total magnetic entropy for N spins will approach $Nk_B \ln(2S + 1)$ at high temperatures where the magnetic susceptibility χ times temperature T approaches the value for an $S = 1/2$ system. The results are compared with numerical calculations based on the finite temperature density matrix

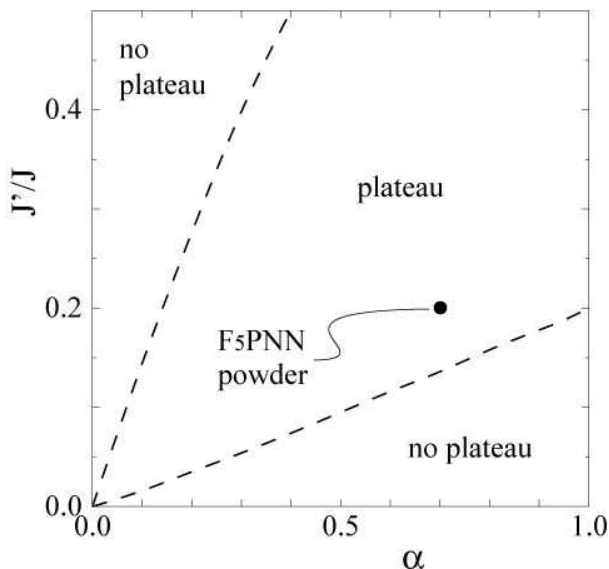


FIG. 5: Alternation ratio α versus NNN interaction J'/J phase diagram at zero temperature at the half value of the saturation magnetization, which is equivalent to the $1/2$ plateau phase diagram in Ref. 17. The filled circle denotes the set of parameters obtained for the F_5PNN powder in this study.

renormalization group (DMRG)¹⁵ as shown in Fig. 4.

The upper panel of Fig. 4 shows the single crystal result and a calculation with the set of parameters $2J/k_B = -5.6$ K and $\alpha = 0.4$, which have been obtained from the magnetic susceptibility and magnetization of a single crystal⁵. The quantitative agreement between the experimental and numerical results means that frustration in the single crystal is too small to detect in the specific heat if it exists.

In the lower panel of Fig. 4, we compare the result of the power with numerical calculations with various parameter sets. It should be noted that the calculation with $2J/k_B = -5.6$ K and $\alpha = 0.4$, which well reproduces the single crystal result, is largely different from the powder result implying the parameters of the powder are not equal to those of the single crystal. Although results for $2J/k_B = -5.6$ K and $\alpha = 0.6$ are better than those for the first parameter set, clear differences appear in the both side of the peak temperature (~ 2 K). Finally, our best result is obtained by assuming a NNN interaction for $J/k_B = -6.8$ K, $\alpha = 0.7$ and $J'/J = 0.2$. We note that the enhanced J and α explain the wider gapless field region of the powder because J and α govern the width of the gapless field region of $S = 1/2$ bond-alternating chains¹⁶. Also, this agreement rules out the possibility that the distinct phase boundary of the powder is ascribed to the disappearance of magnetic moments which comes from the sample deterioration.

The next thing to do is to check whether the set of parameters for the powder is comparable to those in which an IC order is theoretically predicted to appear. Figure

5 shows the different regions of the dominant correlation at the half value of the saturation magnetization in the frustrated alternating chain model as a function of J'/J and the alternation ratio α at $T = 0$. The IC correlation becomes dominant in the same region where the half-magnetization plateau is stable⁴. The set of parameters for the F_5PNN powder, $J'/J = 0.2$ and $\alpha = 0.7$, turns out to be in this region, shown as a filled circle in this figure. This result strongly suggests that the IC correlation is dominant in the powder around the center field of the gapless field region and an IC order exists at very low temperatures.

However, there remains a question why the NNN interaction exists only in the powder. The large pressure dependences of the magnetic susceptibility and specific heat of F_5PNN reported in previous works give us a possible answer to this question^{18,19}. According to these works, α and J increase with increasing external pressure, and even at $P = 0$, mixing powder F_5PNN with Apiezon N grease changes these values. The grease solidifies at low temperatures and gives some stress to the powder inside the solid. Effective pressure by the solidification of the grease is also reported for the powder of another organic compound²⁰.

Generally, an external pressure enhances inter-chain interactions which increase the ordering temperature of the FIMO. Nevertheless, the ordering temperatures of F_5PNN is higher for the single crystal than for the powder which can be under pressure as mentioned above. The strength of an antiferromagnetic interaction in organic magnetic materials depends on how the molecular orbital of an unpaired electron overlaps with the others. Since this orbital spreads rather widely in each molecule, the small variation in the molecular stacking can change the magnetic property drastically²¹. From this point of view, an external pressure most likely changes the molecular stacking in F_5PNN so that the frustrated NNN interaction, which suppresses the ordering temperature, will be enhanced much more than the inter-chain interactions. Very recently, we have seen a more clearly distorted phase boundary for the FIMO around the central field in the specific heat measurement of deuterated F_5PNN powder sample. This result will appear somewhere else. To investigate quantitatively the pressure-induced frustration in this compound, we have proceeded specific heat measurement in magnetic fields under pressure.

V. SUMMARY

We have performed detailed specific heat measurements on the $S = 1/2$ alternating chain material F_5PNN in magnetic fields using a single crystal and powder. The shape of the phase boundary for the field-induced magnetic ordered phases is different between the two sample forms. We have shown the possibility of the pressure-induced frustration in the powder which should lead to field-induced incommensurate ordering around the cen-

tral field besides the Bose-Einstein condensation of triplet magnons, by quantitatively comparing zero-field magnetic specific heats of two samples with numerical calculations based on the finite temperature density matrix renormalization group. A future challenge is the direct observation of the incommensurate ordering.

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